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TECHNICAL NOTE

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MOLLIER DIAGRAMS FOR AIR SATURATED WITH
WATER VAPOR AT LOW TEMPERATURES

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SUMMARY

Two Mollier diagrams relating the thermodynamic properties of air saturated with water vapor in equilibrium with water and with ice at low temperatures are presented. The development of the charts is given and their use in the solution of problems involving thermodynamic processes of mixtures of air and water is explained. A temperature range of 400° to 540° R and a pressure range of 2 to 28 pounds per square inch absolute were chosen in order that the charts would be of greatest utility in considering problems concerned with the icing of aircraft. Several examples that illustrate the use of the diagrams are presented.

INTRODUCTION

In problems involving the thermodynamic properties of a mixture of air and water vapor, the enthalpy and the entropy are often of much greater utility than other more easily determined characteristics of the mixture. The enthalpy and the entropy of a compressible fluid can be conveniently presented as a Mollier diagram that relates these characteristics to other fundamental properties of the fluid.

Two Mollier diagrams for air saturated with water vapor were prepared at the NACA Cleveland laboratory and are presented. The diagrams represent two conditions: One diagram is applicable when vapor-liquid equilibrium exists over the entire temperature range considered; whereas the other diagram should be used if vapor-solid equilibrium exists for subfreezing temperatures and vapor-liquid equilibrium for higher temperatures. These diagrams are useful in dealing with the properties of saturated mixtures of air and water vapor or mixtures containing water in excess of the saturation quantity in various types of thermodynamic process and in the solution of problems involving the icing of aircraft components.

The evaluation of the contributions of the liquid-water or ice content to the enthalpy and the entropy of a system is considered. These contributory terms must be evaluated when mixtures with water in excess of the saturation quantity are considered.

The use of the charts in the solution of thermodynamic and icing problems is illustrated by examples involving several of the various thermodynamic processes for which the charts may be used to advantage.

BASIC ASSUMPTIONS

In the calculation of data for the Mollier diagrams, complete saturation at all points was assumed. This assumption implies the existence of both temperature and phase equilibrium between the vapor and liquid (or solid) states at all points.

The development of the diagrams is based on the applicability of the characteristic equation of a perfect gas to the air and the water vapor over the temperature and pressure range considered and on the use of Dalton's law of partial pressures. Methods for calculating the data required for construction of the diagrams, together with the equations used in the derivation, are presented in the appendix.

The reference temperature and pressure were chosen as 400°R and 14.696 pounds per square inch absolute, respectively. This choice of reference values facilitates the use of the charts in the range of variables covered and integrates the use of the charts with existing tabular data on the thermodynamic properties of air and water. The enthalpy and the entropy of liquid water at the base temperature and pressure were taken as zero.

DESCRIPTION OF CHARTS

The entropy in Btu per pound of air per $^{\circ}\text{R}$ and the enthalpy in Btu per pound of air of the saturated mixture of air and water vapor are plotted as the abscissa and the ordinate, respectively, in the Mollier diagrams (figs. 1 and 2). The chart values are for 1 pound of air plus the amount of water vapor necessary for saturation. The scales used in the construction of the charts are such that the accuracy obtainable is adequate for engineering purposes.

Lines of constant pressure, constant temperature, and constant water-vapor content are also plotted in the figures. Constant pressures are represented by the solid lines with slopes of approximately 1.

Constant temperatures are shown by the dashed lines that are approximately horizontal for the lowest temperatures, but have increasing slopes for the higher temperatures. The dash-dot lines with negative slopes represent constant proportions by weight of water vapor and air (constant-saturation humidity ratios). Plots of the entropy of liquid water and of ice over the temperature range considered are also included in figures 1 and 2, respectively. A curve of the enthalpy of ice in the subfreezing-temperature range is also given in figure 2.

A temperature range from 400° to 540° R and a pressure range from 2 to 28 pounds per square inch absolute are covered by these diagrams.

USES OF CHARTS

The accompanying Mollier diagrams (figs. 1 and 2) are of greatest utility in the consideration of thermodynamic processes where the enthalpy and entropy of air that is continuously saturated with water vapor must be evaluated. The diagrams can be used to obtain the saturation water-vapor content of air under various pressure and temperature conditions, although usually the use of existing tables or charts, which relate these quantities (for example, the pseudoadiabatic charts of the United States Weather Bureau), is more convenient unless the enthalpy or the entropy of the mixture is also desired.

The vapor-liquid chart (fig. 1) or the vapor-solid chart (fig. 2) should be used depending on whether the conditions are such that equilibrium would exist between liquid and vapor phases (supercooled water) or solid and vapor phases at subfreezing temperatures. The differences between the two charts are small, however, because of the low vapor pressures and consequent low saturation contents at subfreezing temperatures. The greatest difference in vapor contents occurs at low pressures; at the point of greatest difference for the range covered by these Mollier diagrams, the saturation vapor content with vapor-liquid equilibrium is approximately 0.019 pound per pound of air, whereas the vapor content with vapor-solid equilibrium at the same temperature and pressure is lower by about 0.0015 pound per pound of air.

The method of using the Mollier diagrams will vary with the individual problem but the following discussion explains the general methods of application. In using the diagrams, two or more of the properties, pressure, temperature, enthalpy, entropy, and water

content of the mixture, will generally be known at the initial thermodynamic state. These known values will enable reading the other thermodynamic properties of a saturated mixture directly from the charts. If the initial mixture contains liquid water or ice, the unvaporized water present will contribute enthalpy and entropy to the mixture. These contributions must be evaluated in order to obtain the accurate enthalpy and the entropy of the mixture. The enthalpy contribution of the liquid water is the product of the specific heat, the liquid-water content, and the temperature difference relative to the base temperature (400° R). The enthalpy contribution due to the ice is the product of the ice content and the specific enthalpy of ice (read from an auxiliary curve in fig. 2). The entropy contribution of the unvaporized water is the product of the liquid-water or ice content and the specific entropy of liquid water or ice at the temperature under consideration (read from the auxiliary curve on the Mollier diagrams). The enthalpy and the entropy of the mixture are then the sums of the enthalpy and entropy terms of the saturated mixture and the unvaporized water.

The path between the initial and final states is determined by the nature of the process under consideration (constant entropy for an isentropic process, constant enthalpy for a throttling process, and so forth). The approximate end point can be read from the Mollier diagram if a single final property is known. Corrections can then be applied to this approximate value for any water undergoing a phase change during the process. The contributory enthalpy and entropy terms are determined for the unvaporized-water content under the new conditions and the chart values corrected by these amounts by the use of successive approximations in order to obtain more accurate enthalpy and entropy values for the mixture. When the unvaporized-water content of a mixture is low, the enthalpy and entropy corrections are often inappreciable and the values read directly from the diagrams may be used with adequate accuracy.

If the water content of the air is less than the saturation quantity, the properties of the mixture can be directly determined from simple thermodynamic relations. When unsaturation occurs during a process, the Mollier diagrams are applicable to that portion of the process in which the total water content of the mixture is in excess of the saturation quantity.

The following examples illustrate some of the problems that can be conveniently solved by means of the Mollier diagrams and also demonstrate the methods followed in calculating different types of process.

EXAMPLES

Stagnation conditions in isentropic flow. - As the first example, the stagnation temperature, pressure, and water-vapor content of a wet air stream is found. The initial conditions of the air stream are as follows:

Total water content, lb/lb air	0.012
Flow velocity, ft/sec	500
Static pressure, lb/sq in. absolute	10
Static temperature, °R	500

The following thermodynamic properties correspond to the initial state (chart values read on fig. 1 at a pressure of 10 lb/sq in. absolute and a temperature of 500° R):

Enthalpy of air plus water vapor (chart), Btu/lb air	33.1
Water-vapor content (chart), lb/lb air	0.0078
Liquid-water content (0.012 - 0.0078), lb/lb air	0.0042
Enthalpy of liquid water (0.0042(T-400)), Btu/lb air	0.42
Enthalpy of mixture (33.1 + 0.42), Btu/lb air	33.52
Entropy of air plus water vapor (chart), Btu/(lb air)(°R)	0.0993
Specific entropy of liquid water (correction chart), Btu/(lb)(°R)	0.222
Entropy of liquid water (0.222 × 0.0042), Btu/(lb air)(°R)	0.0009
Entropy of mixture (0.0993 + 0.0009), Btu/(lb air)(°R)	0.1002

The enthalpy associated with the stagnation condition is the sum of the enthalpy associated with the static temperature and pressure and the enthalpy due to the motion of the fluid or

$$\begin{aligned}\text{stagnation enthalpy} &= \text{static enthalpy} + \frac{V^2}{2Jg} \\ &= \text{static enthalpy} + 4.99\end{aligned}$$

where

V velocity

J Joule's constant

g acceleration due to gravity

Approximate stagnation values can be obtained by neglecting the contribution of the liquid water to the entropy and the enthalpy of the mixture at the end of the process and reading values for the saturated mixture directly from the chart using the stagnation enthalpy and the initial entropy values of the mixture.

Enthalpy of mixture (33.52 + 4.99), Btu/lb air	38.51
Water-vapor content (chart), lb/lb air	0.0102
Liquid-water content (0.012 - 0.0102), lb/lb air	0.0018
Pressure (chart), lb/sq in. absolute	11.5
Temperature (chart), °R	511

More accurate stagnation values are obtained by correcting for the liquid water in the mixture at stagnation conditions.

Entropy of liquid water (0.244 × 0.0018), Btu/(lb air)(°R)	0.0004
Entropy of air plus water vapor (0.1002 - 0.0004), Btu/(lb air)(°R)	0.0998
Enthalpy of liquid water (111 × 0.0018), Btu/lb air	0.20
Enthalpy of air plus water vapor (38.51 - 0.20), Btu/lb air	38.31
Temperature (chart, using final enthalpy and entropy values for air plus water vapor), °R	510
Pressure (chart), lb/sq in. absolute	11.5
Water-vapor content (chart), lb/lb air	0.0101

In the foregoing problem, the values from the approximate procedure are almost the same as the final values. This small difference between the first and second approximations demonstrates that values read directly from the diagrams afford satisfactory accuracy when the liquid-water content is low.

Comparable values for the stagnation temperature and pressure for dry air flowing with the foregoing velocity, temperature, and pressure are

$$\text{stagnation temperature} = \text{static temperature} + \frac{v^2}{2JgC_p}$$

$$= 521^\circ \text{ R}$$

where C_p is the specific heat at constant pressure for dry air and

$$\text{stagnation pressure} = \text{static pressure} \left(\frac{\text{stagnation temperature}}{\text{static temperature}} \right)^{\frac{\gamma}{\gamma-1}}$$

$$= 11.5 \text{ pounds per square inch absolute}$$

where γ is the ratio of the specific heats for dry air. For this problem, the wet and dry stagnation pressures are equal within the accuracy of the chart.

Adiabatic wall temperature. - The adiabatic wall temperature for the foregoing flow conditions is desired. The adiabatic enthalpy at the wall is assumed equal to the static enthalpy plus 85 percent of the kinetic enthalpy.

Static enthalpy, Btu/lb air	33.52
Kinetic enthalpy, Btu/lb air	4.99
Wall enthalpy (33.52 + 0.85 × 4.99), Btu/lb air	37.76

The following values are read from the chart for an enthalpy of 37.76 Btu per pound of air and pressure of 10 pounds per square inch absolute:

Water-vapor content, lb/lb air	0.0103
Liquid-water content, lb/lb air	0.0017
Temperature, °R	507
Enthalpy of liquid water, Btu/lb air	0.18
Enthalpy of air plus water vapor, Btu/lb air	37.58

Because of the low liquid-water content, corrections due to it are insignificant; consequently, the wall temperature is 507° R.

Irreversible throttling. - The final temperature and degree (or percentage) of saturation of a wet mixture following its expansion in a throttling (constant-enthalpy) process is determined. The assumed conditions are as follows:

Total water content, lb/lb air	0.01
Initial pressure, lb/sq in. absolute	20
Pressure following expansion, lb/sq in. absolute	10
Initial temperature, °R	520

At the initial conditions the following values are obtained:

Enthalpy of air plus water vapor, Btu/lb air	38.4
Water-vapor content, lb/lb air	0.0082
Liquid-water content, lb/lb air	0.0018
Enthalpy of liquid water, Btu/lb air	0.22
Enthalpy of mixture, Btu/lb air	38.62

The air becomes unsaturated before expansion is completed; consequently, the pressure and the temperature at which saturation occurs must be found. These values (obtained from the chart, using the total water content and enthalpy of the mixture) are

Static pressure at saturation, lb/sq in. absolute	12.4
Saturation temperature, °R	512

For the expansion beyond the point at which saturation occurs, the mixture is continuously unsaturated. Consequently, the Mollier diagrams are not applicable to this part of the process. Because no further change of phase of any water in the mixture occurs, ordinary thermodynamic relations may be applied; that is, the remaining expansion occurs at constant temperature. The final temperature is therefore 512° R. The saturation vapor content at this temperature and final pressure is 0.0125 pound per pound of air. The saturation is then 0.010/0.0125 or 80 percent.

Ice prevention in engine inlet. - Another example of the use of the charts is the solution of a problem encountered in calculations on the prevention of ice formation in the induction system of an aircraft engine. Assume that an airplane is taking-off under the following conditions:

Total water content, lb/lb air	0.008
Ambient pressure, lb/sq in. absolute	12
Ambient temperature, °R	490

The static pressure in the induction system is assumed to drop isentropically to 8 pounds per square inch absolute. The temperature of the air flowing through the system and the amount of heat that must be added in order to maintain the temperature of the air above the freezing point will be found.

This example is worked for two cases. The first case represents conditions under which the unvaporized water remains in the form of supercooled liquid. The second case represents conditions under which the unvaporized water is in the form of ice until the addition of heat. The heat added is assumed sufficient to raise the temperature to the freezing point and melt all ice in the mixture. In the

first case, figure 1 is used and the resultant values are given in the first column of the following tables; in the second case, the use of figure 2 gives the values in the second column. The free-stream properties of the air are as follows:

	Figure 1	Figure 2
Water-vapor content, lb/lb air	0.0043	0.0043
Unvaporized-water content, lb/lb air	0.0037	0.0037
Enthalpy of air plus water vapor, Btu/lb air	26.6	26.5
Enthalpy of unvaporized water (for column 2, obtained by use of curve in fig. 2 for enthalpy of ice), Btu/lb air	0.33	-0.19
Enthalpy of mixture, Btu/lb air	26.93	26.31
Entropy of air plus water vapor, Btu/(lb air)(°R)	0.0735	0.0732
Entropy of unvaporized water, Btu/(lb air)(°R)	0.0007	-0.0003
Entropy of mixture, Btu/(lb air)(°R)	0.0742	0.0729

If the expansion is considered to occur at constant entropy, the following approximate values in the induction system are obtained:

	Figure 1	Figure 2
Temperature, °R	452	451
Water-vapor content, lb/lb air	0.0013	0.0009
Unvaporized-water content, lb/lb air	0.0067	0.0071
Entropy of unvaporized water, Btu/(lb air)(°R)	0.0008	-0.0009

Corrected values are as follows:

	Figure 1	Figure 2
Entropy of air plus water vapor, Btu/(lb air)(°R)	0.0734	0.0738
Temperature, °R	451	452
Water-vapor content, lb/lb air	0.0012	0.0010
Unvaporized-water content, lb/lb air	0.0068	0.0070
Enthalpy of air plus water vapor, Btu/lb air	13.5	13.7
Enthalpy of unvaporized water, Btu/lb air	0.35	-0.50
Enthalpy of mixture, Btu/lb air	13.85	13.20

(If the desired accuracy requires, these water-content and temperature values may be used as approximate values in order to obtain more accurate values.)

In order to find the amount of heat required to raise the air temperature in the system to the freezing point, a constant-pressure heat addition is assumed to result in a temperature of 491.7°R at a pressure of 8 pounds per square inch absolute with all unvaporized water in the liquid form. Other corresponding values are as follows:

	Figure 1	Figure 2
Water-vapor content, lb/lb air	0.0070	0.0069
Liquid-water content, lb/lb air	0.0010	0.0011
Enthalpy of air plus water vapor, Btu/lb air	30.1	30.1
Enthalpy of liquid water, Btu/lb air	0.09	0.10
Enthalpy of mixture, Btu/lb air	30.19	30.20

The heat addition required to prevent the temperature from dropping below the freezing point during the expansion is equal to the enthalpy difference, or

Heat addition required, Btu/lb air	16.34	17.00
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CONCLUSIONS

The two Mollier diagrams presented are of benefit in the solution of wet-air problems. The temperature and pressure ranges covered are such that the diagrams are readily applicable to many thermodynamic and icing calculations. Considerable saving in time can be effected by the use of the diagrams rather than involved formulas in the solution of many wet-air problems.

Lewis Flight Propulsion Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, July 8, 1948.

APPENDIX - DEVELOPMENT OF CHARTS

The values of enthalpy, entropy, and water-vapor content of saturated mixtures were determined for use in construction of the Mollier diagrams in the following manner:

Pressure, temperature, and vapor content. - The reference pressure chosen for the Mollier diagrams was the standard NACA sea-level static pressure (14.696 lb/sq in.). A base temperature of 400° R was chosen in order that the data on the thermodynamic properties of air given in reference 1 could be directly used in the preparation of these charts and in order that these charts could be used in conjunction with reference 1 without transferring from one reference temperature to another. This choice of reference temperature also facilitates the use of the charts because the temperature range in which the charts will be applied lies above the base temperature and the necessity of working with both positive and negative enthalpy values is thereby minimized.

In the following calculations, the air and the amount of water vapor required to saturate it are considered separately. For a given temperature, the saturation pressure of water vapor was determined. The saturation pressures for the vapor-liquid equilibrium were obtained from table 244 of reference 2 (p. 563). The corresponding values for the vapor-solid equilibrium were obtained from table 264 of reference 2 (pp. 600 and 601). The partial pressure of air was determined as the total pressure minus the saturation vapor pressure. The specific volume of the air V_a was then obtained from the relation

$$P_a V_a = RT$$

where

P_a partial pressure of air

R gas constant for air

T absolute temperature

The specific volume of water vapor for the same temperature and total pressure (sum of partial pressure of air and of water vapor) was obtained from a similar equation. Because the air and the water vapor occupied the same volume, the ratio of the specific volume of air to the specific volume of water vapor represented the water-vapor content of a saturated mixture at a given pressure and temperature in pounds of water vapor per pound of air.

Enthalpy and entropy of vapor-saturated air. - The enthalpy of the air was read directly from table 1 of reference 1 (pp. 4 and 5). The entropy of the air S_a was obtained from the relation (reference 1, p. 57)

$$S_a = \phi - \frac{R}{J} \log_e \frac{P_a}{14.696}$$

where

$$\phi = \int_{400}^T \frac{C_p}{T} dT$$

was obtained directly from table 1 of reference 1.

The values of the enthalpy and the entropy of water vapor were calculated and then, with the water-vapor content at saturation known, the enthalpy and the entropy terms due to this amount of water vapor were obtained. Values of the enthalpy of water vapor for temperatures above freezing were obtained directly from table 1 of reference 3, page 28, and corrected to the reference temperature of 400° R. This correction was effected by adding to the tabular values the enthalpy (relative to the base temperature) of liquid water at the freezing point. In the determination of this correction, the value of C_p for liquid water in the range from 400° R to the freezing point was assumed to be 1.0 Btu per pound water per °R. Values of the enthalpy of water vapor at subfreezing temperatures were obtained by subtracting from the freezing-point value of the enthalpy of vapor the enthalpy change accompanying the lowering of the temperature of the vapor from the freezing temperature to temperature T , or

$$H_{v,T} = H_{v,f} - C_{p,v}(T_f - T)$$

where H is the enthalpy, the subscript v denotes the vapor phase, and the subscript f indicates that the quantity is evaluated at the freezing temperature. In applying this equation, the value 0.4427 Btu per pound per °R was chosen for $C_{p,v}$ after consideration of the available experimental data in the range from 400° R to the freezing point.

Entropy values for water vapor S_v (relative to the reference temperature of 400° R) at temperatures between 400° R and freezing were obtained from the relation

$$S_v = \frac{\Delta H}{T} + \log_e \left(\frac{T}{400} \right)$$

where ΔH is the change in enthalpy during evaporation at temperature T . In the calculations, ΔH was considered as the difference between the enthalpies of liquid water and of vapor at temperature T . For entropy values of the vapor at temperatures above freezing, values taken from table 1 of reference 3 were used after they were corrected to the base temperature by adding to the tabular value the entropy of liquid water at the freezing point relative to the reference temperature of 400°R .

The values of the enthalpy and the entropy of the mixture per pound of air were then obtained as the sums of the enthalpy and entropy terms, respectively, due to 1 pound of dry air and the quantity of water vapor required to saturate it. These data were then plotted as the ordinate and the abscissa in figures 1 and 2. Constant-pressure and constant-temperature lines were plotted on the diagrams in order to relate the thermodynamic qualities, enthalpy and entropy, to the physical state of the mixture. Saturation water-vapor contents were determined as functions of the pressure and the entropy by means of cross plots. Lines of constant water-vapor content were then plotted on the figures.

Entropy of liquid water. - The auxiliary curve for the entropy of liquid water in figure 1 is based on the equation

$$dS = \frac{dH}{T}$$

For a base temperature of 400°R and an assumed value of C_p of 1.0 for the range of temperatures up to the freezing temperature, the entropy becomes

$$S = \log_e \left(\frac{T}{400} \right)$$

In determining the entropy for higher temperatures, values from table 1 of reference 3 were used in the equation

$$S = S_f + S_T$$

where S_f is the entropy at the freezing point relative to 400°R and S_T is the value of the entropy from reference 3. In figure 2, the portion of the entropy curve for liquid water at temperatures above freezing is the same as the corresponding portion of the curve of figure 1.

Enthalpy and entropy of ice. - In figure 2, the enthalpy and entropy of ice at subfreezing temperatures are given in auxiliary curves. Data for both curves in the temperature range below freezing were obtained from table 5 of reference 3 (p. 76).

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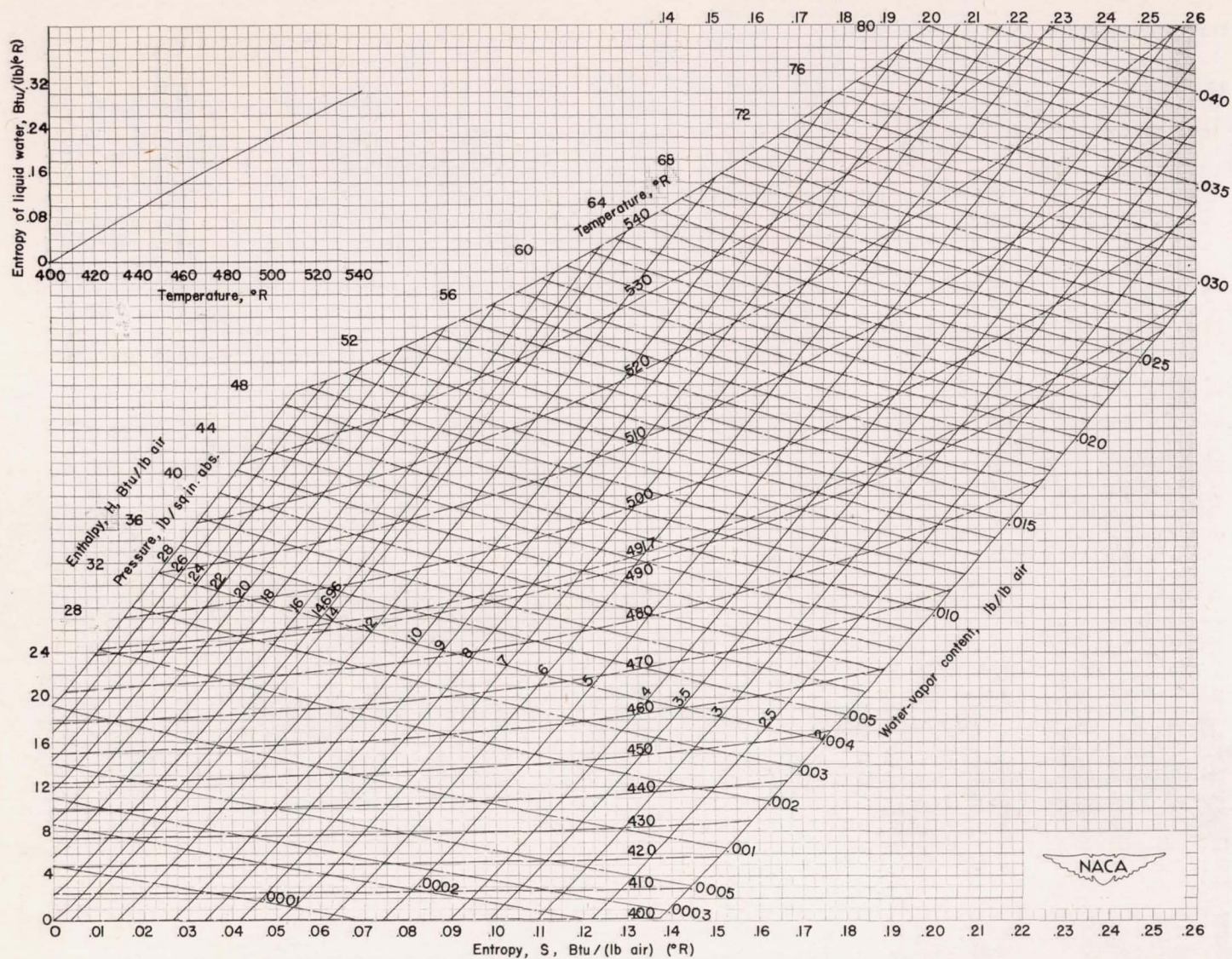


Figure 1. - Mollier diagram for air saturated with water vapor at vapor-liquid equilibrium conditions. (A 17- by 22-in. print of this figure is attached.)

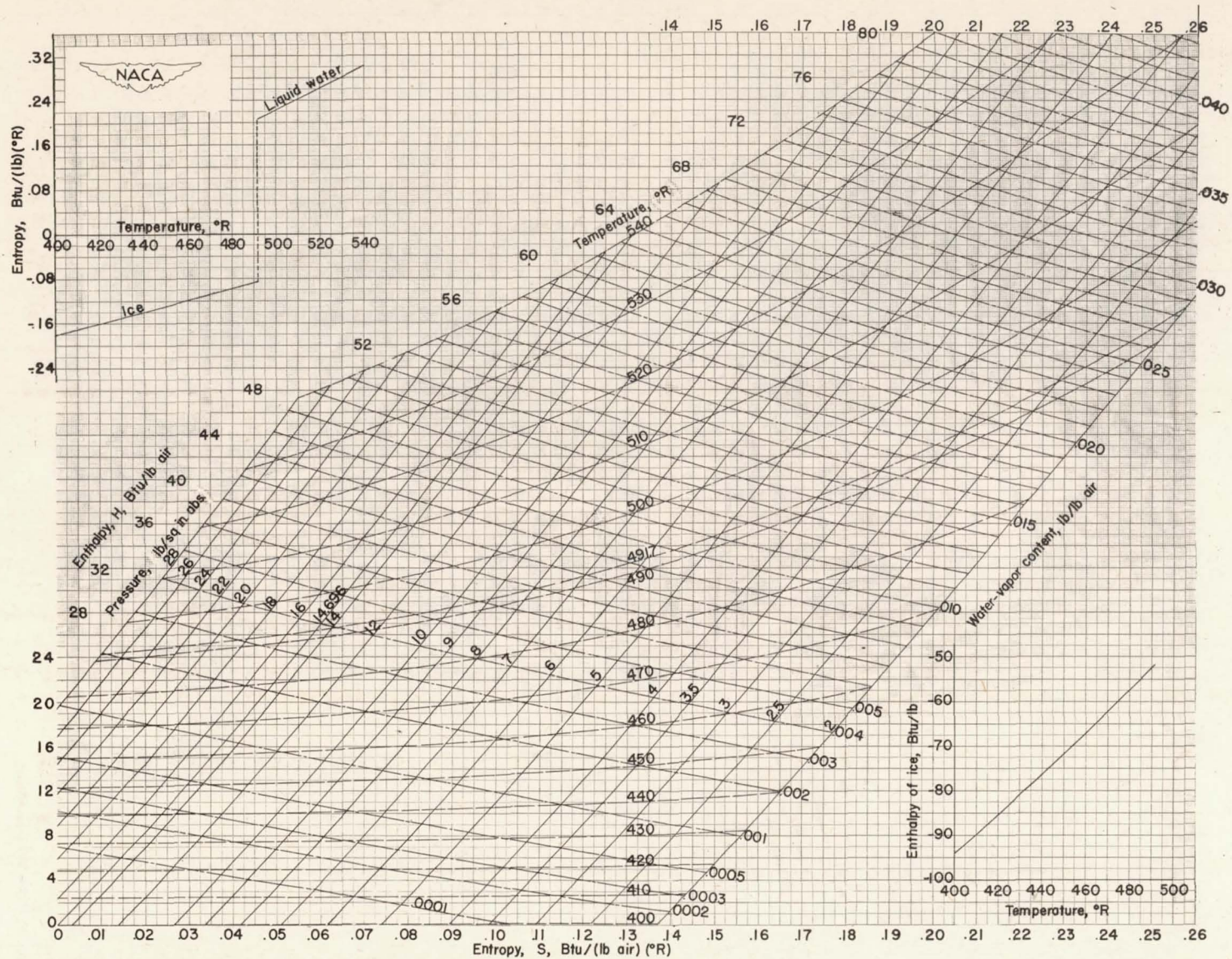


Figure 2. - Mollier diagram for air saturated with water vapor at vapor-solid equilibrium for subfreezing temperatures.
(A 17- by 22-in. print of this figure is attached.)

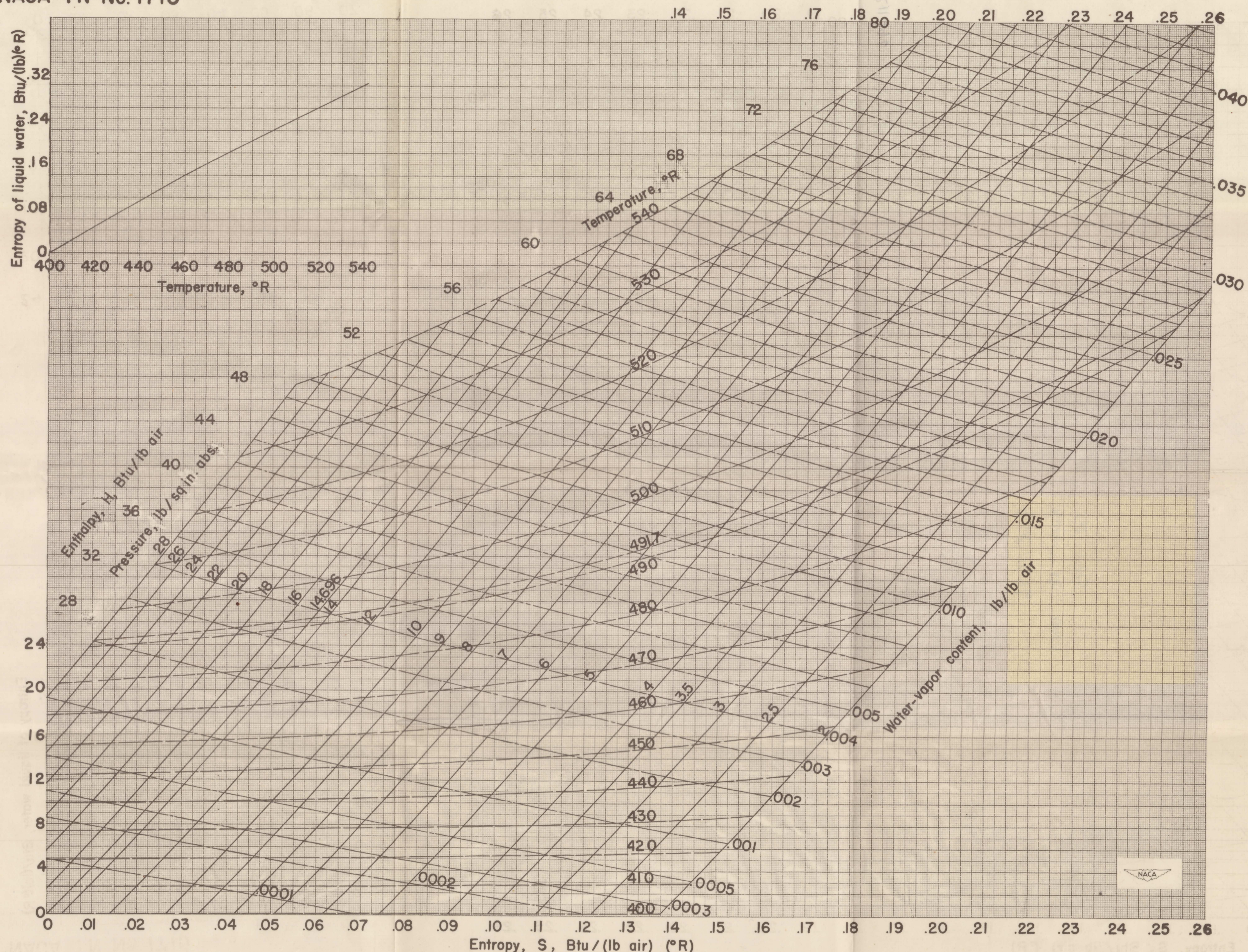


Figure 1. - Mollier diagram for air saturated with water vapor at vapor-liquid equilibrium conditions.

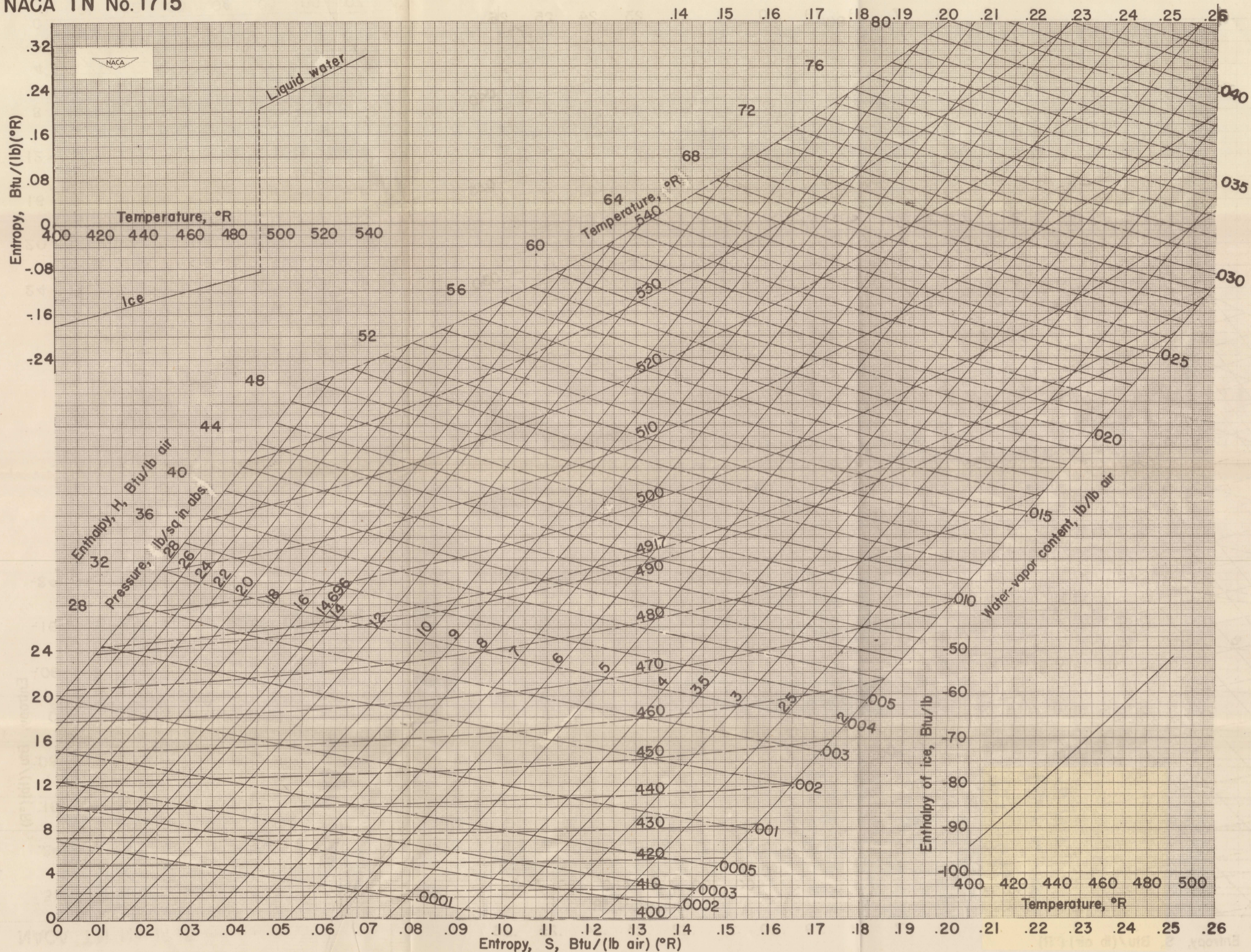


Figure 2.- Mollier diagram for air saturated with water vapor at vapor-solid equilibrium for subfreezing temperatures.